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EFFECTS OF AIR/NITROGEN CURE ON AN ACETYLENE TERMINATED QUINOXALINE THERMOSET SYSTEM

Polymer Branch
Nonmetallic Materials Division

June 1981

Final Report for Period March 1980 to December 1980

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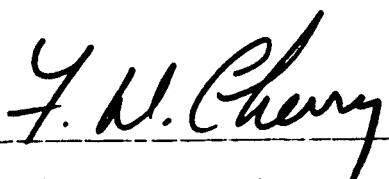


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The issues raised from the findings of this work were discussed.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFWAL/ML Project Scientist. Co-authors were Dr. C. Y-C Lee, Materials Laboratory/AFWAL/MLBP, and Mr. J. D. Henes, University of Dayton Research Institute.

This report covers research conducted from March 1980 to December 1980.

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SECTION I
INTRODUCTION

The Air Force has an interest in the development of acetylene-terminated (AT) resins as a new technology to form high performance structural materials (Reference 1). One of the resins synthesized in-house has already been chosen for further development and pound quantities prepared for this purpose. Air curing effects on the physical properties of some AT systems are recognized (Reference 2) based on other in-house works, yet no systematic study of this effect has been undertaken.

In another TICA study of a blend of BA-DAB-BA (Reference 3) and mono-ATP (Reference 4), an anomaly from conventional thermosetting systems was observed; namely, that a thermal scan of an uncured specimen will yield a double-peak α -component. At first, this was thought to be either an experimental artifact or a complication due to the blending. Further investigation failed to substantiate either one of these contentions. Additional experiments showed that such behavior is present in neat BA-DAB-BA and (95/5) ATS (Reference 5) as well. So, obviously, this anomaly is common among the AT systems.

A series of TICA experiments was then initiated using BA-DAB-BA to further investigate this anomaly and the effects of curing on this two-peak feature. The air/nitrogen effect was also incorporated. The intent of this report is to present the findings thus far.

The experimental results are very interesting and a four-reactions interpretation, which can satisfactorily account for all the features observed is forwarded. Recognizing that this interpretation may not be unique in being able to explain the observations, cares are taken to separate the experimental results from the interpretation as much as possible in this report so other workers who will attempt to present an alternate interpretation can go through the data with ease.

SECTION II
EXPERIMENTAL

The TICA sample preparation procedure has been described elsewhere (Reference 6). The measurements were made with the Rheometrics Mechanical Spectrometer (RMS). The frequency of measurement was kept constant for all experiments (1.6 Hz, 10 rad/sec).

Normally, the temperature programmer on the RMS unit presently installed in this laboratory is coupled with the Rheophaser which controls the mechanical measurements. A special electronic clocking device was built to decouple the two units. The temperature programmer was run in a local mode with temperature increase in steps of 2°C per minute. The clocking device then synchronized the Rheophaser to take measurement every minute. The clocking device was programmed so the measurement was taken just before the temperature step increase. This way the temperature increasing rate is a truly 2°C/min rate, and the data do not contain the noises caused by the temperature step increase.

All specimens were cured exclusively with the RMS environmental chamber. Air or nitrogen was used as the convecting medium. The specimen was placed in the chamber at room temperature and the same temperature increase procedure used in isothermal curing measurements (Reference 6) was employed to bring the chamber up to the curing temperatures. An earlier attempt to cure specimens in a Vac-line oven gave unacceptable data scattering and poor correlation between specimens. This was because of the long time required for the Vac-line to equilibrate at the controlling temperature after each disturbance, like opening the oven door.

All scanning experiments were repeated with a scan-down in temperature at the same scanning rate after the upper temperature limit was reached.

SECTION III

RESULTS

1. EFFECTS OF SCANNING UNDER AIR/NITROGEN ENVIRONMENT

An uncured TICA specimen of BADABBA was scanned in temperature under nitrogen atmosphere at a rate of $2^{\circ}\text{C}/\text{min}$ with the procedure described in the previous section. The result is shown in Figure 1.

The scan-up result can be explained by a four-stage scheme forwarded by Lee and Goldfarb (Reference 7). The scheme is designed for experiments where T_g is not a constant during the measurements. The scanning rate of such an experiment (dT/dt) is assumed to be a constant. Depending on the rate of change of the T_g value (dT_g/dt), the experiment can be at either one of the following four stages:

- (I) $dT_g/dt = 0$,
- (II) $0 < dT_g/dt < dT/dt$,
- (III) $0 < dT/dt < dT_g/dt$;
- or (IV) $dT_g/dt < 0$.

Briefly, Stage I is when the glass transition temperature is a constant. Stage II and Stage III are when the T_g is increasing; but they are further distinguished by comparing with the constant scanning rate. Stage IV is when the T_g is actually decreasing in value. A rate conversion point is defined as the point when the experiment is transiting from Stage II to Stage III. At such a point, the scanning rate, dT/dt , is the same as the T_g increasing rate, dT_g/dt ; and the time derivative of the parameter ($T-T_g$) is zero.

In Stage II, $(T-T_g)$ is increasing, but in Stage III, the parameter is decreasing. The scheme is modified here to include a Stage R which is a region where the specimen remains at the rate conversion point. In the R Stage, the $(T-T_g)$ parameter is a constant and the dynamic responses do not appear to change with temperature.

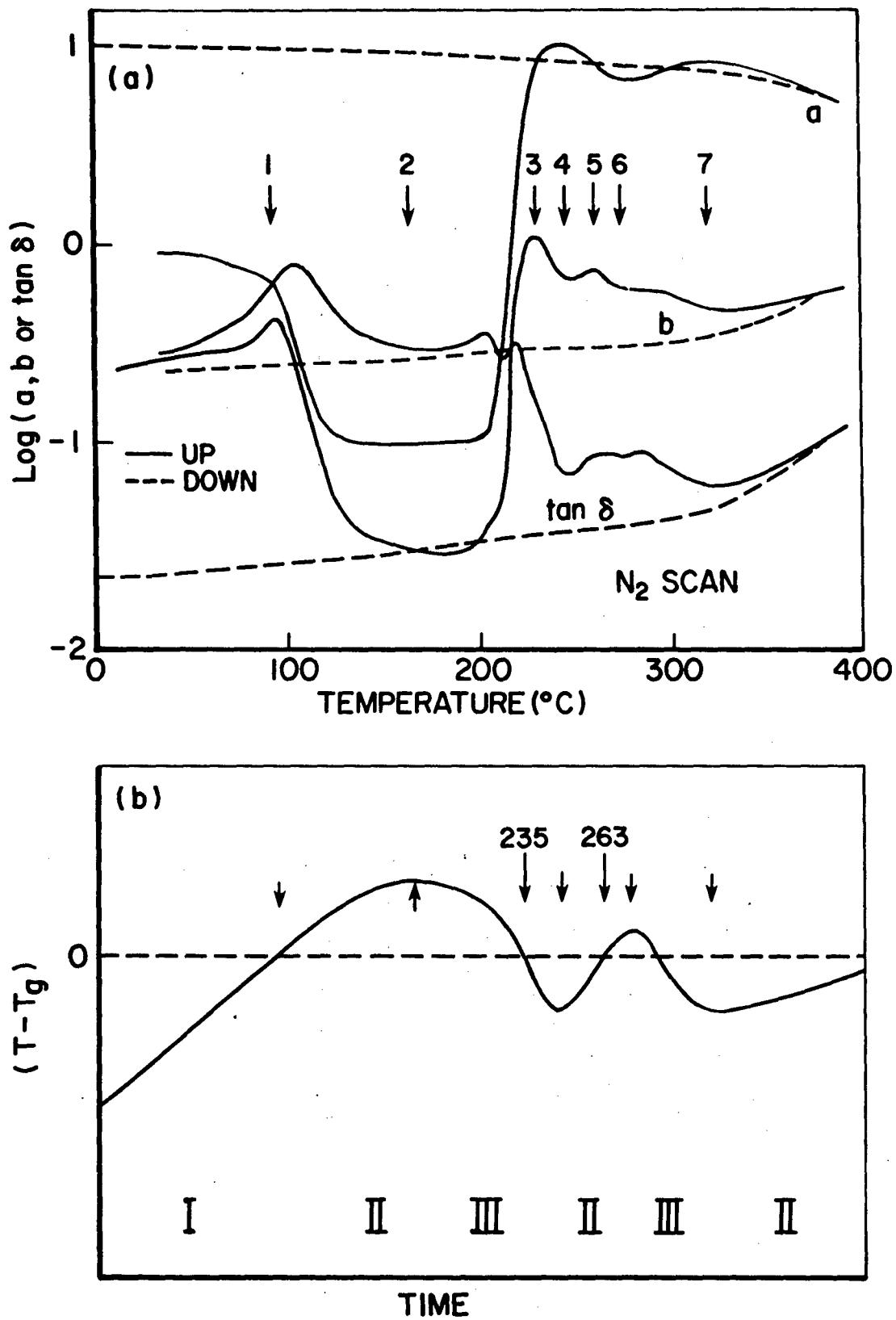


Figure 1. Nitrogen Scan Results of an Uncured Specimen

Thus, for a given scanning rate, the curing rate is increasing in the order of Stage II, Stage R, and Stage III. An experiment can be classified according to the sequence of the Stages appearing during the scan. Curing rates in different experiments can be compared by noting the stages involved.

The scan-up result in Figure 1 can be classified as a I-II-III-II-III-II experiment. The corresponding (T-Tg) curve is shown in Figure 1-b. At the beginning of the experiment, Tg was not changing, so the experiment was in Stage I, and the (T-Tg) parameter was increasing at the experimental scanning rate. At point 1, the b-component was showing a peak maximum corresponding to the uncured Tg of the system. Between points 1 and 2, the system was in the liquid state. Somewhere in that region, additional cure started to occur and the experiment proceeded into Stage II. At about 200°C, the a-component rised sharply, accompanied by the corresponding b and tan δ peaks. The system was vitrifying; and the (T-Tg) parameter was decreasing to a negative value. The experiment was obviously in Stage III; and had passed the first rate conversion point. The second rate conversion point was encountered at point 4. The experiment was back in Stage II, and the system was again above Tg after point 5. A third rate conversion point was encountered at point 6, with the system back in Stage III again. The fourth rate conversion point was at point 7. After that, the system was in Stage II, and eventually Stage I. Thus the experiment can be described as a I-II-III-II-III-II type (Reference 7).

The scan-down result indicated that the a-component had decreased with the additional cure, and the Tg of the system had been advanced to more than 390°C. One can argue that the decrease in the a-component is due to thermal degradation. Yet, TGA results did not indicate weight loss until over 550°C and more importantly, the Tg is increasing instead of decreasing. On scan down, the fact that all the b peaks and tan δ peaks have vanished supports the interpretation that they are due to the additional cure effect.

It is not uncommon for an uncured or a partially cured specimen to give a I-II-III-II-I type result which involves only two rate conversion points. The first would of course be due to additional cure; the second would be the result of depletion of reactive sites. The result described above is the first known example of a I-II-III-II-III-II type experiment. This feature is not exclusive to the BADABBA resin; similar results have been observed with ATS and a BADABBA/ATP blend (Reference 8). So it seems that the four rate conversions feature is common among AT systems.

Scanning the specimen in air produced a different result (Figure 2). The experiment should be classified as a I-II-III-II-R-II-III experiment. The corresponding (T-Tg) plot is shown in Figure 2-b. The system went through the early I-II-III Stages like the nitrogen scan experiment, with the vitrification peak occurring at about the same temperature. After that, the system never went back above Tg. The second a-component peak in the nitrogen scan experiment was reduced to a plateau; and the valley between the a peaks had disappeared. This changes the succeeding II-III-II Stages of the nitrogen scan experiment to become II-R-II Stages. The b and tan δ features observed in the nitrogen scan result were absent and the presence of the additional cure was only indicated by the plateau of the a-component.

An additional Stage III was observed in the air scan result, and the corresponding rate conversion point (the fifth one) was at 355°C. The decrease of the b-component above that temperature was the result of the decrease of the parameter (T-Tg). This is verified by the scan-down result which indicated that the Tg had been advanced to well above 390°C.

2. EFFECT OF CURING UNDER AIR/NITROGEN ENVIRONMENT

A TICA specimen of BADABBA was cured under nitrogen at 160°C for 24 hours. The thermal scan of the specimen under nitrogen is shown in Figure 3. Comparing with the nitrogen scan of the uncured specimen Figure 1, it is obvious that the liquid stage was gone. The specimen was glassy during the whole experiment, with a limited degree of softening at about 285°C. The curing at low temperature had changed the experiment

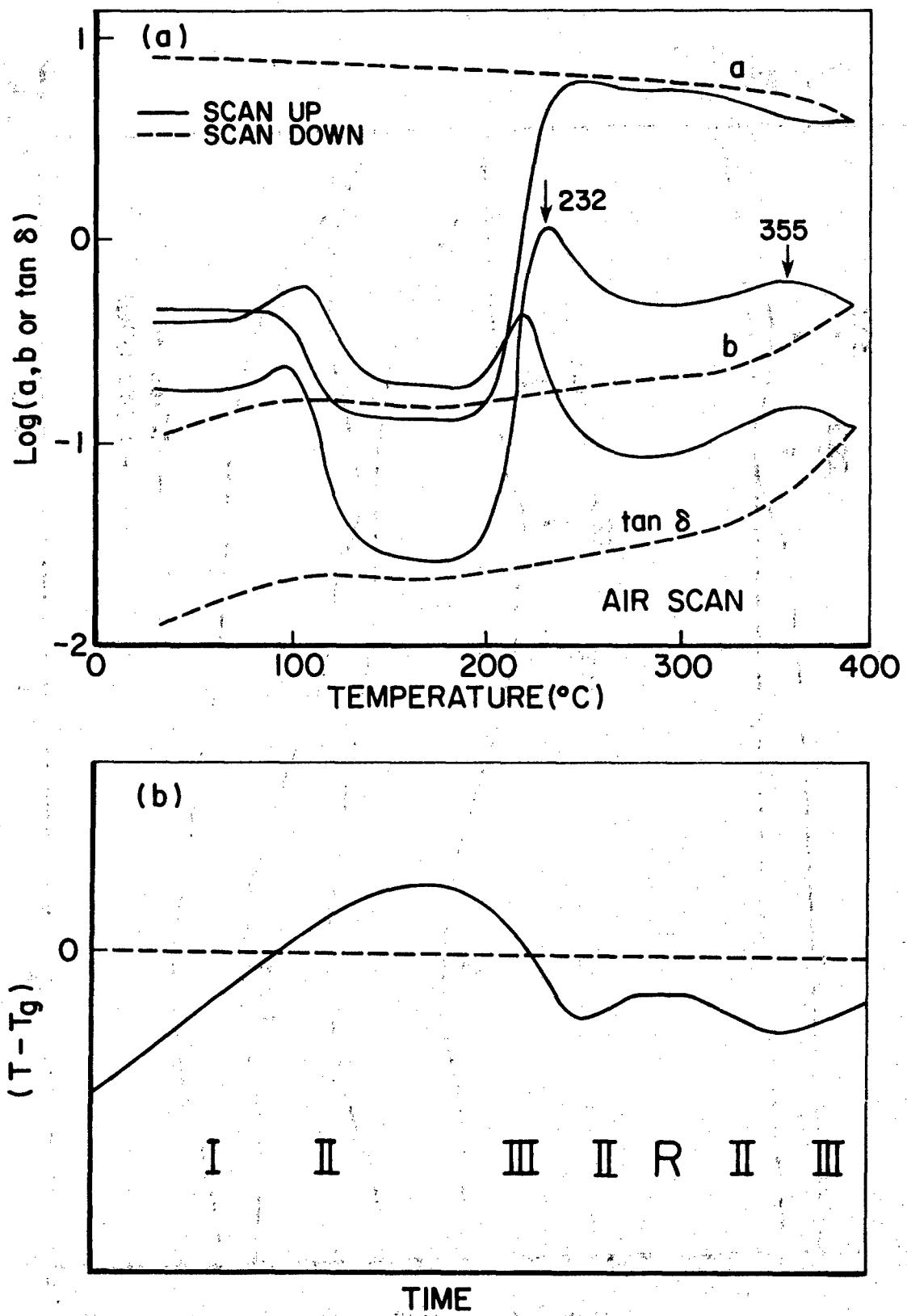


Figure 2. Air Scan Result of an Uncured Specimen

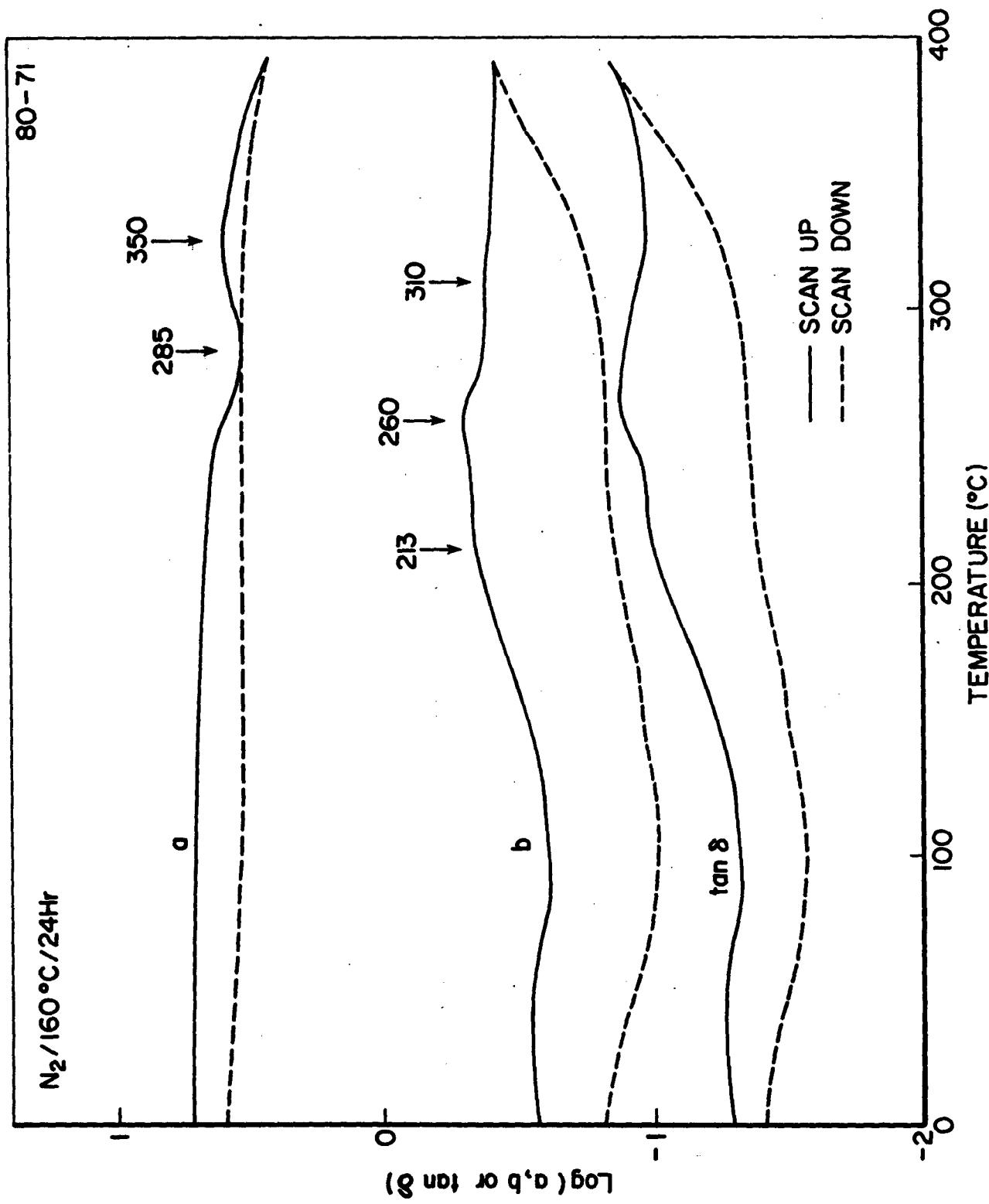


Figure 3. Scan of a Specimen that has been Cured at 160°C for 24 Hrs Under Nitrogen

to a I-II-R-II-III-II experiment. The third rate conversion point was obviously at 285°C and the fourth at 350°C.

Again, the result is not the type of I-II-III-II-I experiment one observes with epoxy samples. The hum of the b-component at 213°C means additional cure was occurring at that temperature. The curing rate was as fast as the scanning rate in the next 30° region so the parameter (T-Tg) was almost a constant or in the R Stage, with little changes in the a and b components. Then the specimen went above Tg at 260°C, indicating that the curing rate had slowed to a value smaller than the constant scanning rate. The experiment momentarily slipped back into Stage II, and then proceeded into Stage III after 285°C. It is difficult to justify that the reaction that slowed down at 260°C is the same reaction that increases the Tg so rapidly around 300°C.

The a-component decreased after 350°C during the scan-up. The b-component changed relatively little in that region. The scan-down result suggested the Tg was advancing during the scan up, and as a result, the a-component had also decreased. So the negative slope in the a-component above 350°C in the scan-up result can either be interpreted as a Stage II effect, where (T-Tg) was a decreasing function, or as a Stage III effect, where the additional cure caused the a-component to decrease.

The scan-down result showed the Tg of the system after the scan was above 390°C; and all the features exhibited by the a- and b- components in the scan-up were caused by additional cure.

Another specimen was cured at 160°C for 24 hours in an air environment. The subsequent thermal scan result under nitrogen is shown in Figure 4. The result is different than that of Figure 3. The scan-up curves give the appearance of a three-phase system with three distinct regions of a-component decrease, each accompanied by a corresponding b peaks. However, the result should actually be classified as a I-II-R-II-R-II-I experiment. Additional curing of a partially cured specimen giving an appearance similar to a two-phase system had been observed before (Reference 7). In this case, the process was repeated twice due to two different reactions.

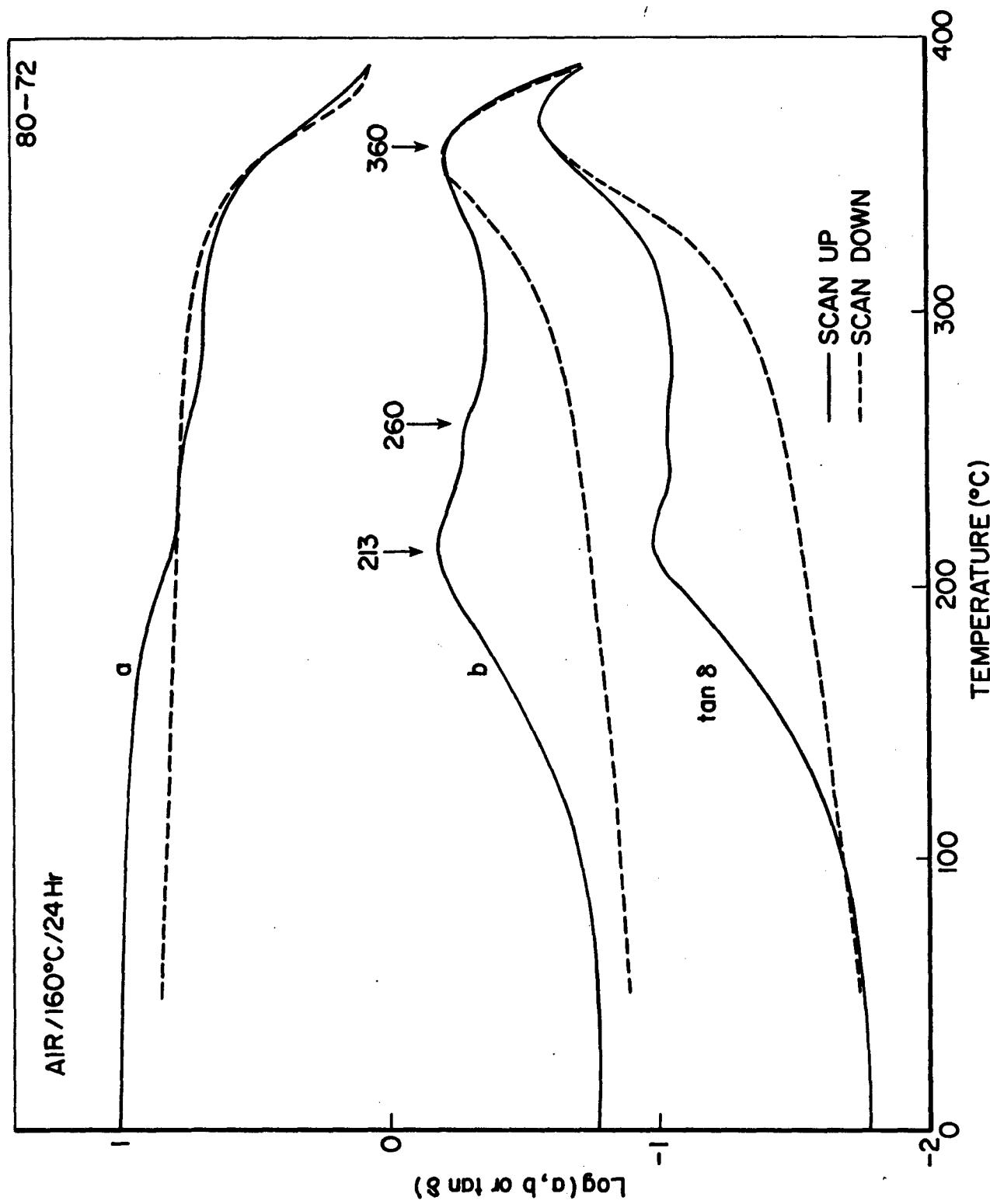


Figure 4. Scan of a Specimen that has been Cured at 160°C for 24 Hrs Under Air

The first b peak maximum was at 213°C, the same temperature as the first b shoulder in the nitrogen cure result. The peak in the air cure was much more intense, and the drop in the a-component in that region was much more significant. The peaks in both the air cure and the nitrogen cure results signified an abrupt change in the curing rate, and both were occurring at the region where $(T-T_a)$ was negative. The air cure specimen however, was having the event occurred at a larger $(T-T_g)$ value or closer to the glass transition temperature. This could either be interpreted as the additional curing rate in the air cure specimen being slower than that of the nitrogen-cure, thus the $(T-T_g)$ parameter increasing with a steeper slope; or that the air-cure specimen had a lower T_g to begin with.

A b shoulder was again observed at 260°C, which could be interpreted as an indication of the limitation of the first reaction, like depletion of reactive groups. After additional cure at about 300°C, the $(T-T_g)$ parameter increased to a positive value (above T_g) at 360°C. The second reaction was less intense than the corresponding nitrogen-cured result as indicated by the Stage R effect rather than the Stage III effect in that region.

The scan-down result retraced the scan-up curves in the region above 350°C. This means in that region the system was back in Stage I during the scan-up. The completely cured T_g of this particular specimen was 360°C.

Two specimens had also been cured at 200°C for 1 hour, with one being under nitrogen and the other in air. The subsequent scans of these specimens under nitrogen are shown in Figures 5 and 6. The features are very similar to those that had been cured at 160°C for 24 hours (Figures 3, 4). Again, peak maxima of the b-component at about 210°C were observed, followed by another at about 260°C. The final T_g of the nitrogen cure specimen was above 390°C, but that of air cure was at 375°C.

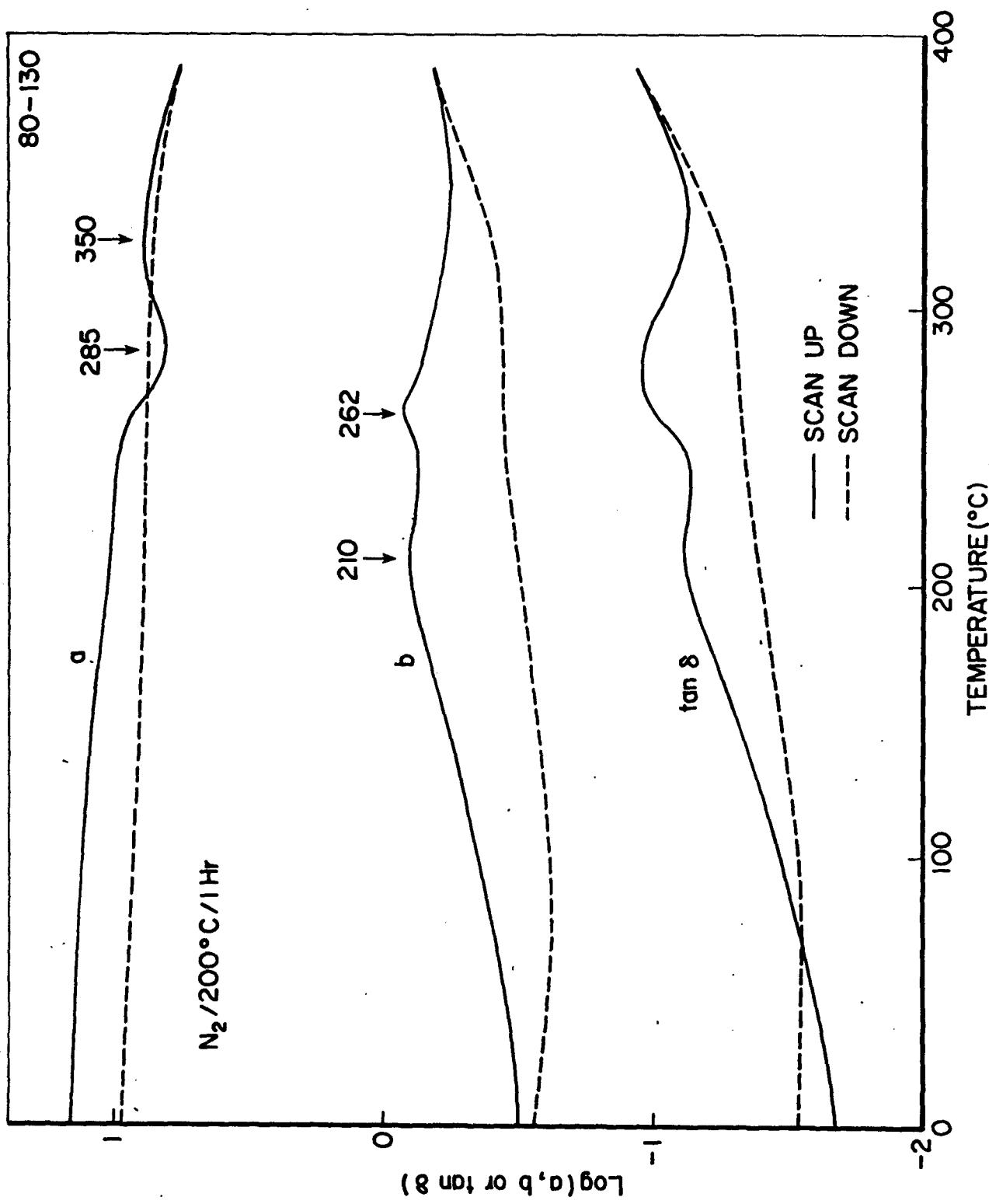


Figure 5. Scan of a Specimen that has been Cured at 200°C for 1 Hr Under Nitrogen

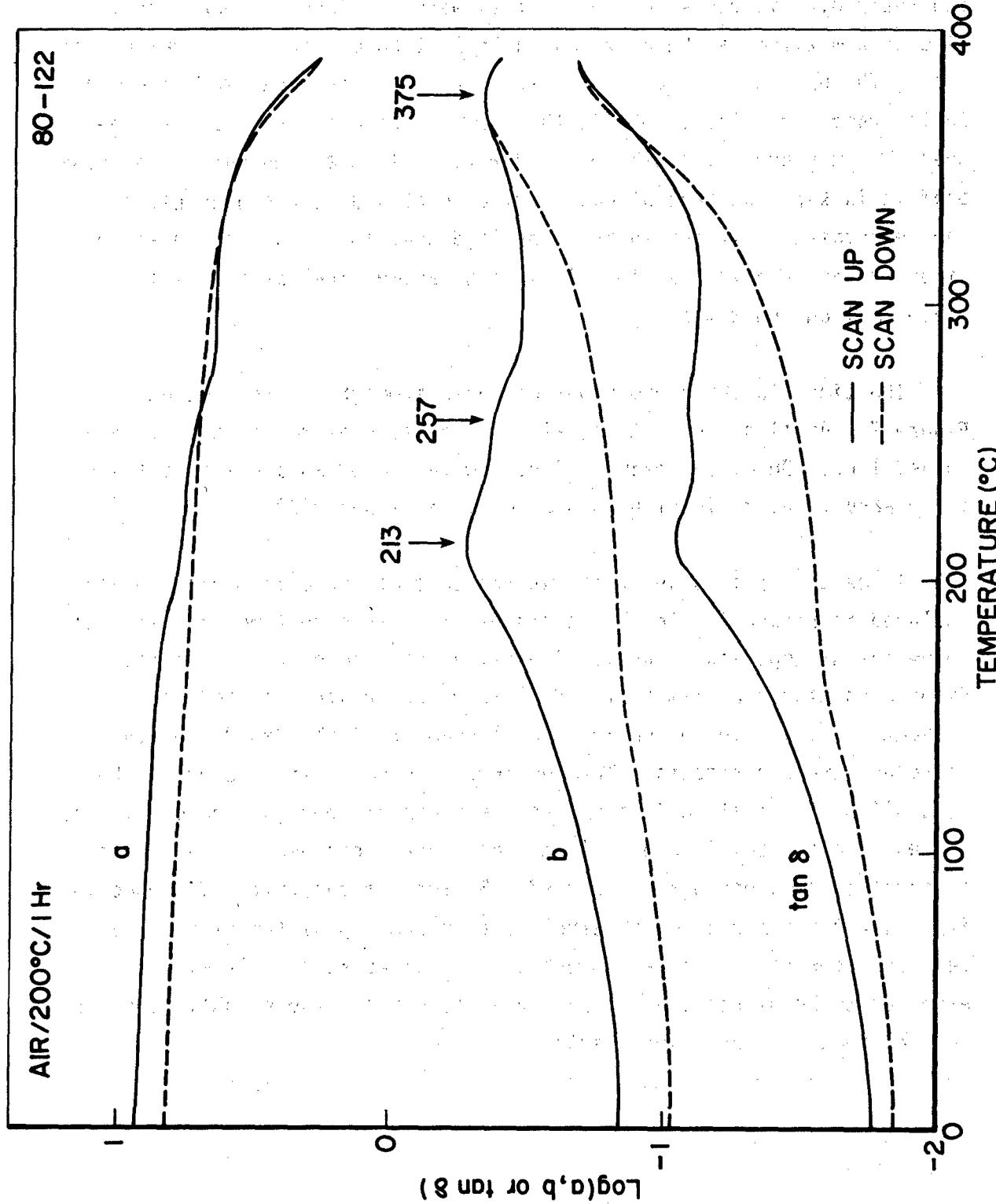


Figure 6. Scan of a Specimen that has been Cured at 200°C for 1 Hr Under Air

3. ISOTHERMAL CURE TIME TO b-MAXIMUM

TICA specimens were cured isothermally at different temperatures and their dynamic mechanical properties were continuously monitored. The time to b-maximum can be noted as an indication of the isothermal curing rate. The procedure used was already outlined elsewhere (Reference 6). In the range of 200°C to 350°C, the reaction rate is very fast so the heat-up times are not negligible. However, if the temperature increase profile is kept constant at each curing temperature, reproducible results can be obtained. It should be emphasized that in cases where heat-up times are not negligible, the times to b-maximum are not the real isothermal curing times.

The times to b-maximum under nitrogen atmosphere are plotted in Figure 7. At first inspection, all the points seem to be falling on a curved line. On closer examination, however, one can argue that there is an abrupt change in slope of the curve at about 250°C.

Three data points using air as the controlling atmosphere are also included in Figure 7. In all instances, the air-cure times are slightly below the nitrogen-cure curve. The differences however are slight. Evaporated nitrogen from a liquid nitrogen reservoir was used as the convection medium in the environmental chamber of the RMS during the nitrogen cure experiments. The low temperature gas was heated to the controlling temperature in a heat-element compartment just before it was forced into the sample area. In the air cure experiment, however, room temperature compressed air was used. Because of the vast difference in input air temperatures, the temperature increase profiles of the two sets of experiments can be different. The air-cure profile will be expected to be higher and can possibly account for the slightly shorter curing times in those experiments.

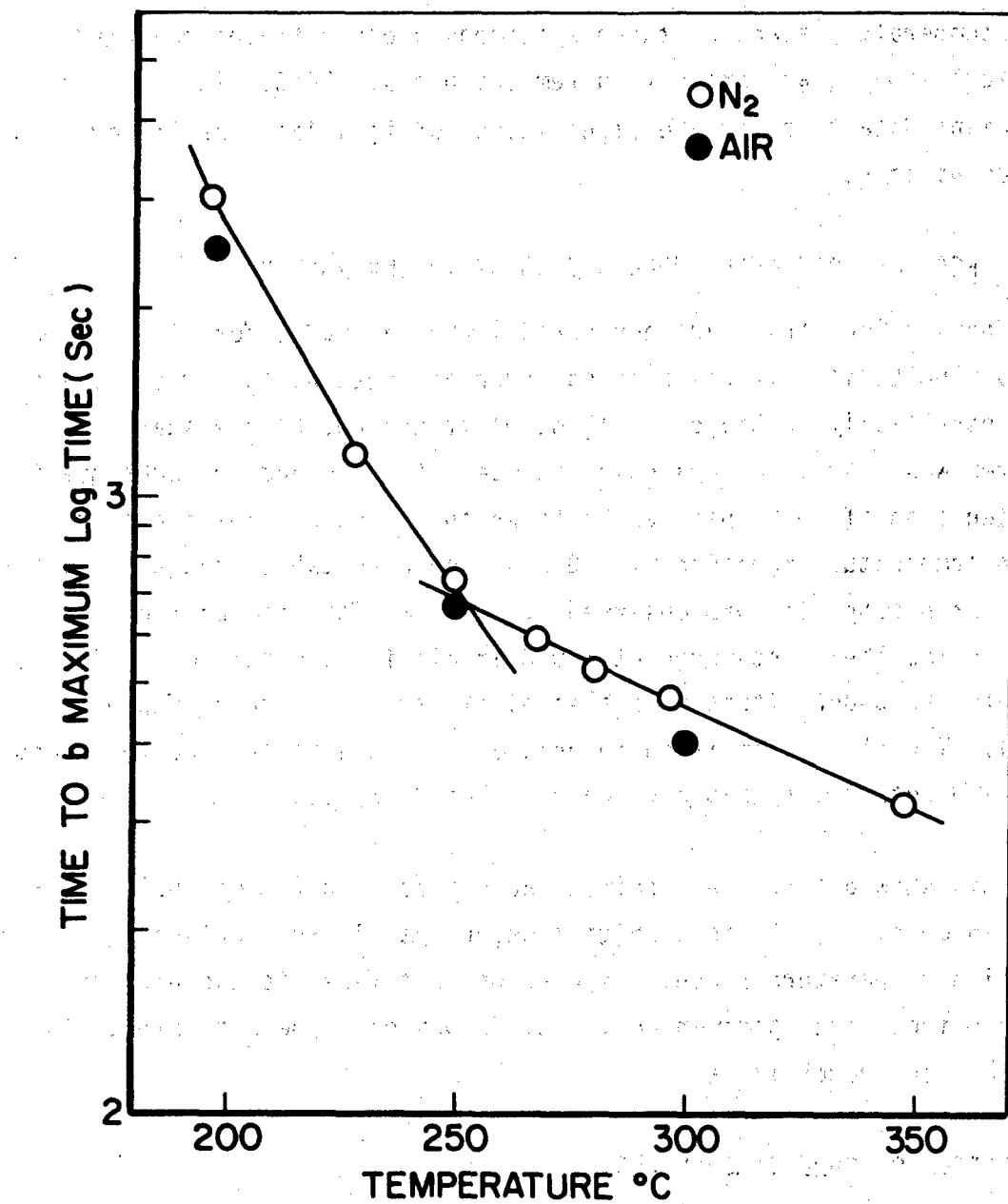


Figure 7. Time to b Maximum vs Cure Temperature

The samples that were cured in air at 200°C, 250°C, and 300°C were quenched to stop the air curing shortly after the b-maximum peaks; then they were post-cured in nitrogen at 350°C for half an hour. The subsequent temperature scans of these specimens under nitrogen revealed an identical final glass transition temperature at 380°C. There are insufficient data to claim the significance of this fact, or it may just be a coincidence.

4. EFFECT OF POST CURE UNDER NITROGEN/AIR ENVIRONMENT

The specimen that had been cured in air at 160°C for 24 hours had a Tg of 360°C after it was scanned under nitrogen up to 390°C and was found essentially in Stage I ($dTg/dt=0$) at the end of the scan. The specimen was post-cured again in nitrogen at 380°C and the subsequent nitrogen scan of this specimen is shown in Figure 8. The glass transition temperature remained at 360°C and no detectable change in either the a- or b-component was observed before and after the post cure. The specimen was then post-cured at 380°C in air for another hour. The subsequent scan under nitrogen is also displayed in Figure 8 (the dotted lines). The glass transition temperature had been increased to beyond 390°C and both the a- and b-components had decreased.

This showed that the specimen had reached a Tg (∞) of 360°C under nitrogen cure. The Tg is so high however that it is overlapping with the oxidation temperature range. If care was not taken to exclude the oxidation effect, the specimen would have appeared to be not completely reacted even though it was.

5. EFFECT OF CURE TIME IN AIR

Four specimens were cured at 200°C in air for various lengths in time (1/2 hr, 1 hr, 2 hrs, and 24 hrs). The thermal scans of these specimens under nitrogen are shown in Figure 9 (1/2 hr), Figure 10 (2 hrs); and Figure 11 (24 hrs) - (the 1 hr result has already been shown in Figure 6).

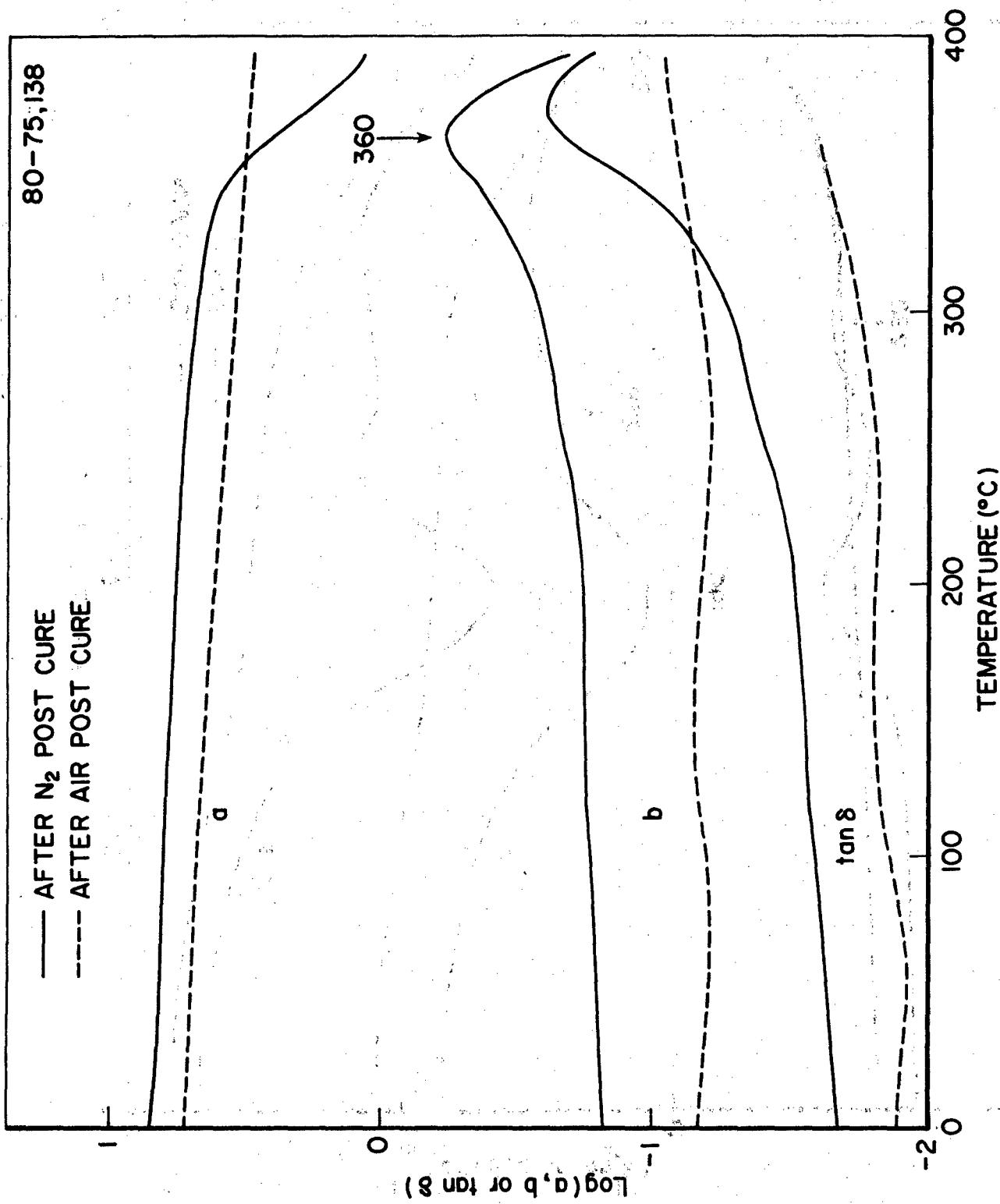


Figure 8. Scans After Postcuring in Nitrogen and Air

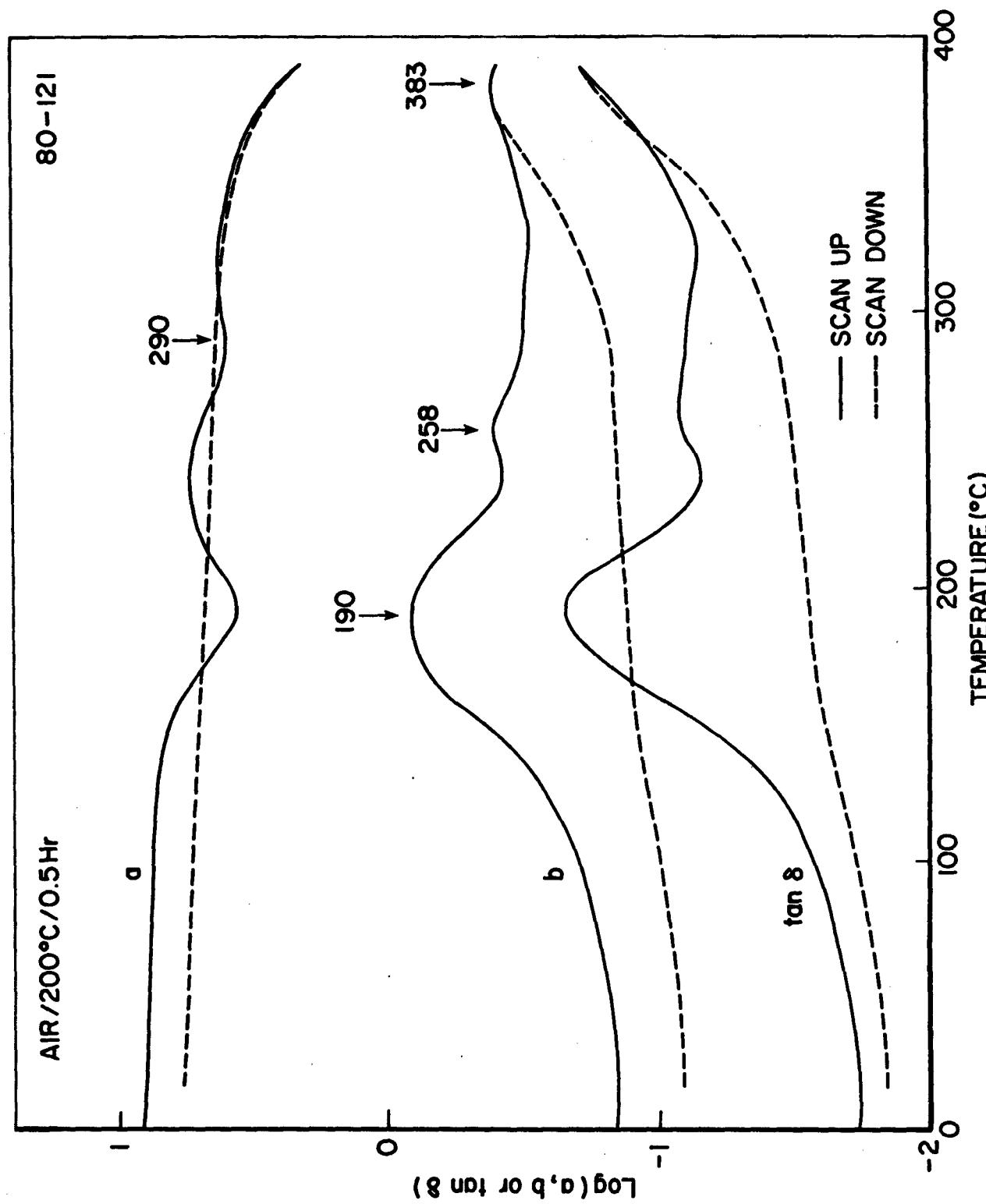


Figure 9. Scan of a Specimen that has been Cured at 200°C for a Half Hour Under Air

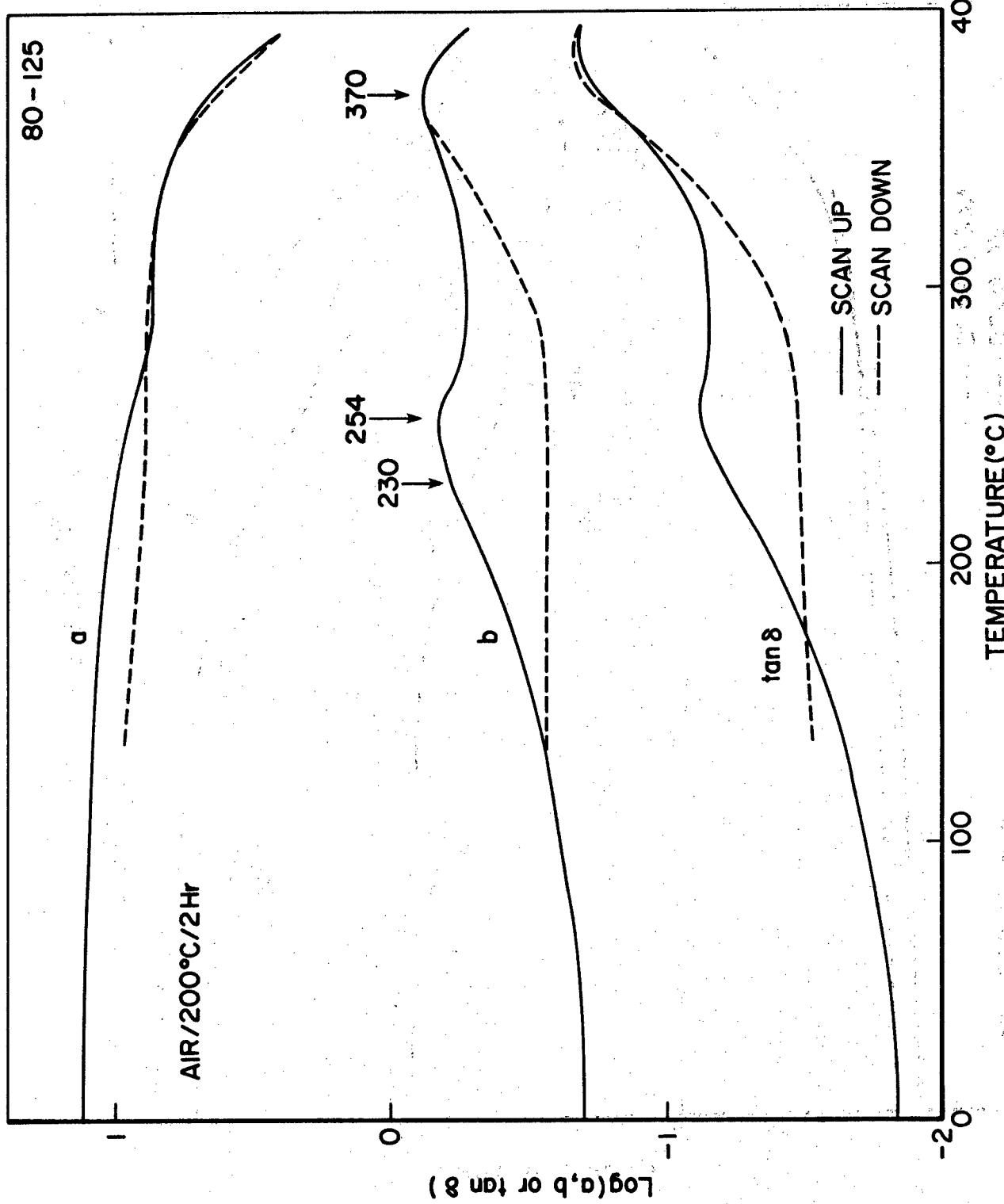


Figure 10. Scan for a Specimen that has been Cured at 200°C for 2 Hrs Under Air

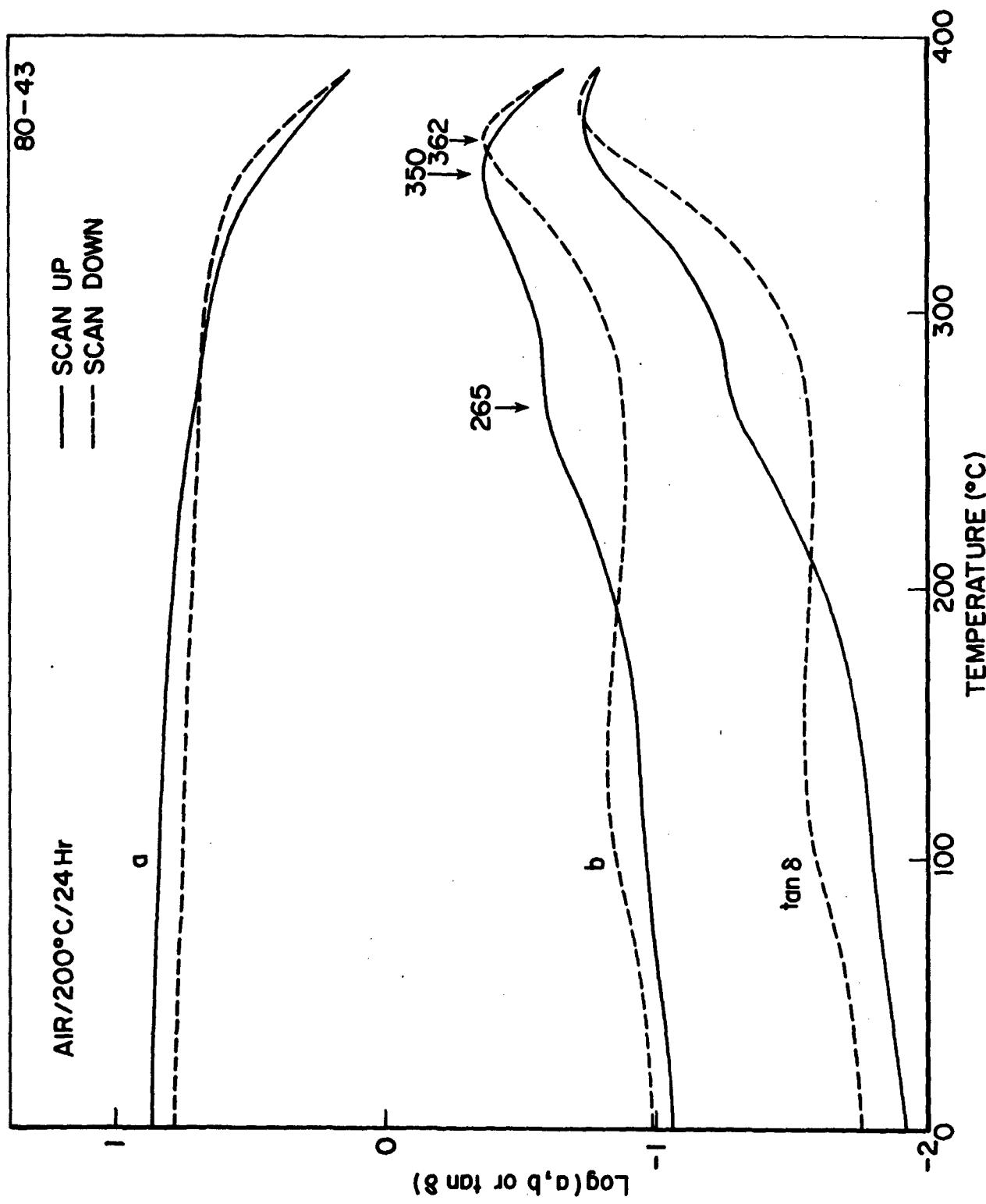


Figure 11. Scan of a Specimen that has been Cured at 200°C for 24 Hrs Under Air

The 1/2-hour cure result in Figure 9 is clearly a I-II-III-II-III-II-I experiment. It shows two minima in the a-component. The first minimum at 195°C was also accompanied by a b-component maximum and can easily be identified as the first rate conversion point. At the second Stage II, the b-component went through a maximum at 258°C before it converted back into Stage III at 290°C. The peak at 258°C is again a sign of the limitation of the first reaction as discussed before. The specimen was finally in Stage I again at the end of the scan with a final Tg of 383°C.

The 1-hour cure result (Figure 6) has been discussed before. It is worthwhile to restate here that the first b-component maximum had been increased to 213°C with a shoulder of the b-maximum showing at 257°C. The valleys of the a-component had been reduced to plateaus and the final Tg was lowered to 375°C.

The 2-hour cure result (Figure 10) showed that the first valley of the a-component was not detectable any more but a b-component shoulder was still observed at 230°C. Again a b maximum was shown at 254°C accompanied by the drop of the a-component. The final Tg was lowered to 370°C. The scan-down result suggested that the specimen was in Stage I at the end of the scan-up.

The 24-hour cure result (Figure 11) showed that the first b maximum had disappeared. A b-component shoulder remained at 265°C. An apparent glass transition peak was observed at 350°C in the scan-up. The scan-down result however, showed that the glass transition temperature had moved up to 362°C. The experiment was not in Stage I at the end of the scan-up.

SECTION IV

DISCUSSION

From the data presented in the previous section, it is obvious that curing under different conditions will yield specimens with permanent changes as evidenced by the different $T_g(\infty)$ the systems attained.

Combining all the data, we can empirically hypothesize that there are four distinct effects of curing. Each effect may be a distinct reaction itself. The natures of these reactions are not known, so they are labeled alphabetically as A, B, C, and D. A summary of these effects is listed in Table 1.

Reactions A and B can occur under nitrogen. Reaction A is occurring at low temperature and Reaction B is at a higher temperature. The rate of Reaction B is not comparably faster than the scanning rate of $2^{\circ}\text{C}/\text{min}$ until the temperature is above 270°C . The nitrogen scan experiment (Figure 1) best exemplifies the two reactions. The first II-III-II Stages are typical of a further reaction during a temperature scan; and the total reaction rate is slowed down (second Stage II) because of depletion of reactive groups. The glass transition observed after the Stage III is usually also the final T_g of the system, or $T_g(\infty)$ (Reference 7). The fact that Stage III occurred again after the Stage II implies either the slowing down of the reaction rate in Stage II is not due to the depletion of reactive groups that causes the first Stage III, or that the second Stage III is the result of a different reaction. The result of the additional Stage III is a double-peak appearance in the a-component.

The appearance of the double-peak in the a-component during a temperature scan is first observed in a TICA specimen of a blend of mono-ATP and BADABBA. At first, the double peak feature was thought to be either an experimental artifact or a complication due to a blend of two materials. The feature is experimentally reproducible. TGA experiments did not show weight loss in the region of 270°C , which means the second transition of Stage II to Stage III cannot be due to the loss of low molecular weight

materials which act as plasticizers in the specimen. A thermocouple was embedded in another specimen, and no anomaly was observed between the temperatures of the sample chamber and the interior of the specimen during the scan. This rules out the notion of the temporary softening in the Stage II being a result of an intense exotherm due to the curing reaction. The two-peak feature was again observed in ATS and BADABBA. All these favor the explanation of two different reactions which are common to most acetylene terminated systems.

The fact that the two reactions can be so vividly separated by a valley of the a-component means the two reactions must have very different activation energies. One can argue that B will necessarily follow A if B is a reaction of the products formed in A. But without the difference in activation energies, the two reactions would be merged together, and mechanical properties scan should not be able to separate their effects. The notion that two separate reactions are involved is further supported by the appearance of two intersecting lines in the time to b maximum plot.

If the specimen is cured and also scanned in nitrogen, the final Tg of the specimen is above 400°C. Because we cannot observe the Tg (∞) in these cases, it is not certain if the Tg (∞) is affected by the low temperature curing. Judging from the intensity of the second a-component peak, reaction B doesn't seem to be affected by the initial curing under nitrogen (Figures 3, 5). The effect of reaction B is not only increasing the Tg (∞); the a-component is also decreased.

The other two reactions required the presence of air. The effect of D is best demonstrated by the air-scan experiment (Figure 2) and the post cure experiments (Figure 8). Only at high temperature is the reaction rate of D comparable with the scanning rate. The most likely explanation of reaction D is oxidative crosslinking. The crosslinking can be at the backbone of the resin (the quinoxaline part), the "chain" resulted from the reaction of the acetylene, or the "joint" that joined two resins together as a dimer through the acetylene reaction. Regardless

of the nature of reaction D, its effect is to raise the final Tg to above 400°C and at the same time lower the a-component.

The fact that reaction D is significant only at high temperature does not mean it doesn't occur at lower temperatures. The "significance" in observation is highly dependent on the experimental time scale, in this case, the scanning rate. At lower scanning rate or long time exposure at use temperature, the temperature should be lower where reaction D is significant.

Reaction C is not directly observed in this series of experiments, but its effect can be observed by comparing with the nitrogen cure data. There is no a priori reason to say whether reaction C is different or the same as the reaction D, but the effect observed in this series of experiments is different, so it is treated accordingly. However, one can say that they are unlikely to be the same, considering that reaction C can occur at 140°C, while reaction D is not observed until 370°C.

Looking over the thermal scan results, we can see a persistent pattern of behavior in the b-component. First there is a shoulder or peak which resulted from the additional curing because of the competing effects of the curing rate and the constant experimental scanning rate on the parameter (T-Tg). This peak is labelled as Tc because it is a sign of the additional cure. It can also be used as a rough indicator of the extent of cure prior to the scanning experiment. The reason it is a rough indicator is that additional cure probably occurs before the Tc is reached.

The second and third peak are the Tg (∞) of reaction A and B respectively, so they are labeled as TgA (∞) and TgB (∞). For the TgB (∞) that are below 400°C, the value obtained during the scan-up is usually the same as that during the scan-down with the exception of the specimen that had been cured at 200°C in air for 24 hours. All Tc, TgA (∞) and TgB (∞) are listed in Table 2 along with the curing conditions.

The $TgA(\infty)$ values do not appear to be affected by the curing conditions. The average of all the $TgA(\infty)$ values listed is 260°C , with the scattering within a $\pm 5^{\circ}\text{C}$ range. The scatter is within the experimental errors and the uncertainty in identifying the peak locations due to the sloping characteristics in the region. Air curing did not affect its value, and neither did the cure time nor the cure temperature.

It is interesting to note that in a previous study of BADABBA (Reference 9), the Tg increase as a function of cure time at 200°C was measured with the calibration Technique (Reference 10). The Tg was found to reach a value of $250 \pm 10^{\circ}\text{C}$ after about 2 hours of curing and stop increasing. At the time, the diffusion control of the reaction was thought to be the cause of the Tg remaining at a constant value. In light of the finding here, it is possible that the previous experiment was reaching the limit of reaction A.

Reaction C does not have effect on $TgA(\infty)$, but its effect on reaction B can readily be demonstrated. The a-component scans as a function of initial curing time and temperature are reproduced in Figure 12. The second peak of the a-component is diminished with increasing cure time in air, and also with increasing cure temperature. The feature doesn't seem to be affected if the curing was done under nitrogen. This implies that reaction C, which requires air, will prohibit reaction B.

The Tc and $TgB(\infty)$ as functions of cure time and cure temperature are plotted in Figure 13 and 14 respectively. The Tc , being a rough indication of the extent of reaction A, increases with increasing temperature and time as expected. The $TgB(\infty)$, however, decreases with the higher temperature or longer time exposure in air during the initial curing. This is another indication of reaction C prohibiting reaction B.

The data presented here will not shed light on the nature of the reactions. But it is safe to assume reaction A is the reaction of the acetylene groups. If we further assume that reaction B and C do not

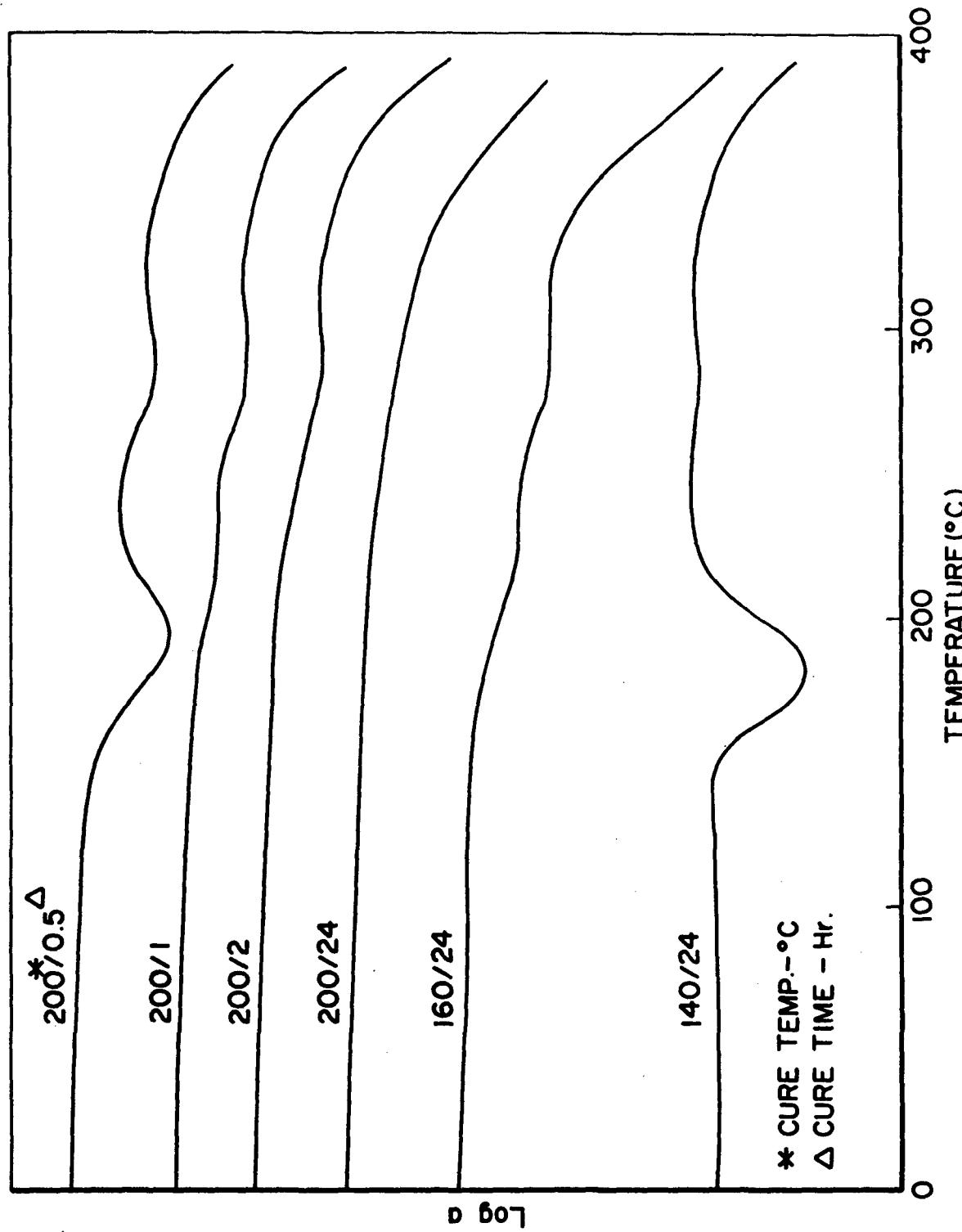


Figure 12. a-component Curves After Different Curing Conditions

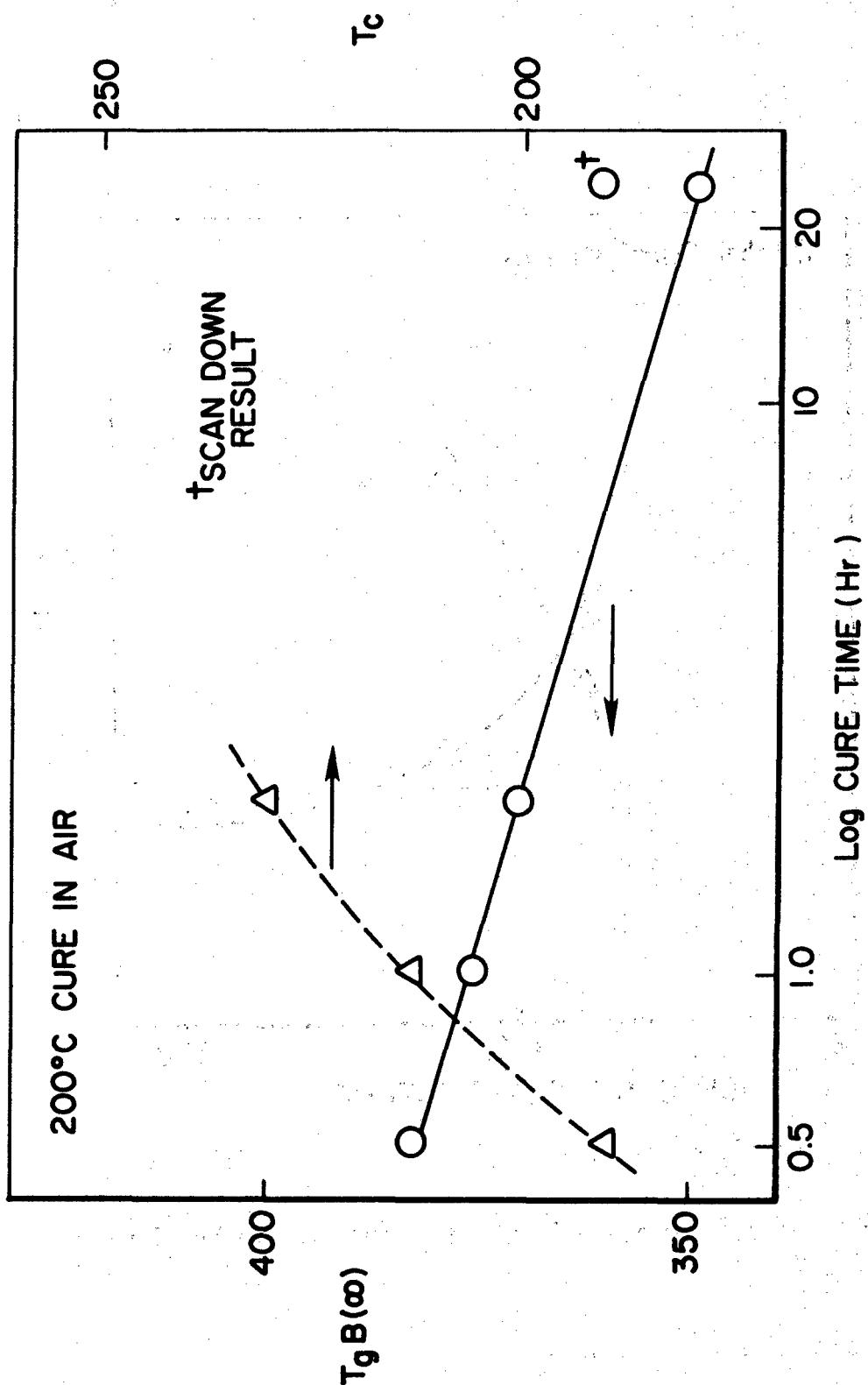


Figure 13. T_c and $T_g B(\infty)$ vs Cure Time at 200°C

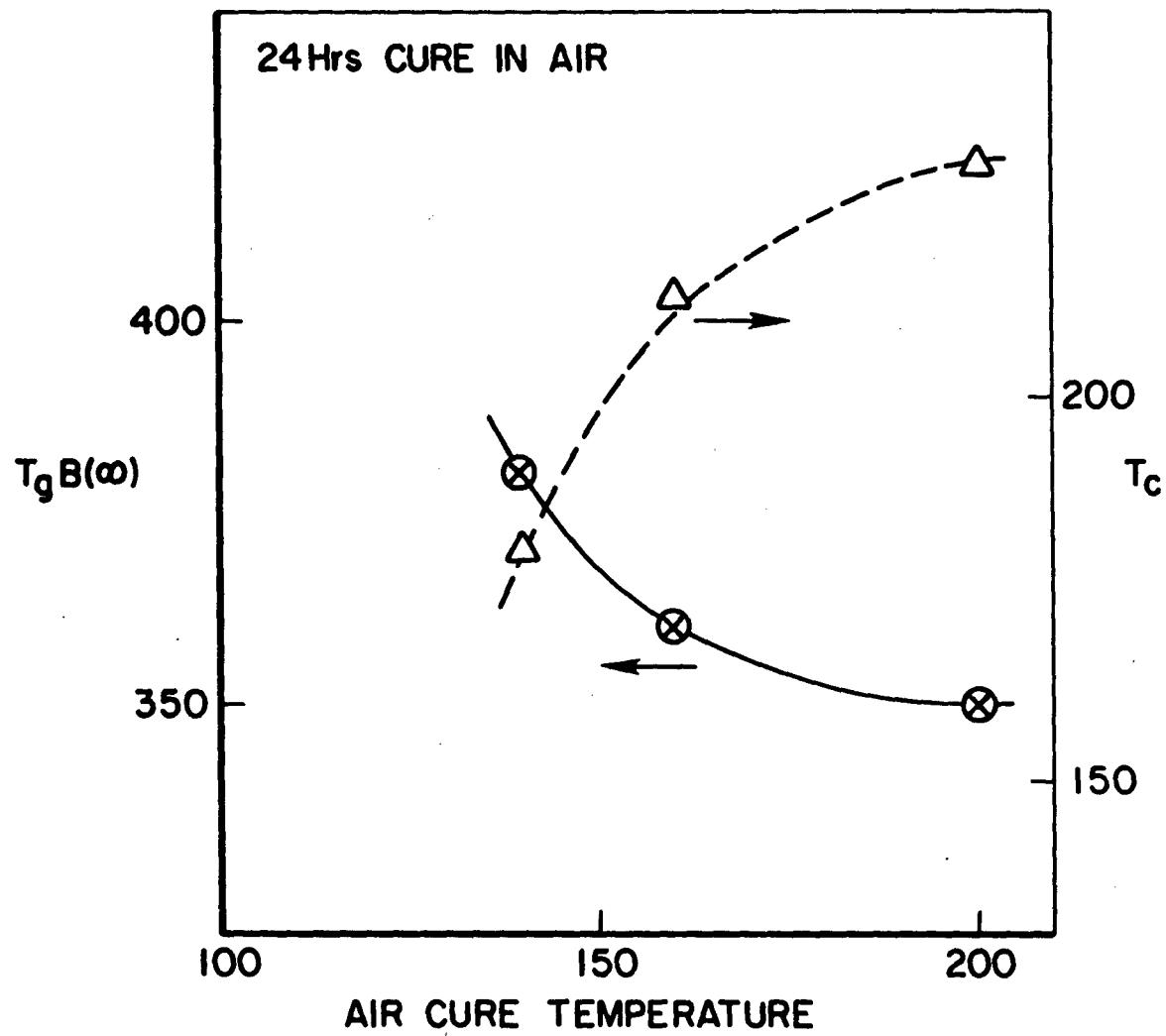


Figure 14. T_c and $T_g B(\infty)$ vs Cure Temperature for 24 Hrs Cure

involve the quinoxaline part, they are either the reaction of the acetylene groups, or the reaction of the products of A. Based on these assumptions, four possibilities can be listed by labeling the reactants and products of the reactions with Roman numerals:



In each case, I, the acetylene groups, is reacted in A to form II, whatever it is; then B and C involve either the reaction of I or II. They all seem to have inconsistencies when compared with the experimental data. Any specific suggestions as to the nature of the reactions, however, can likely be fitted into one of the four possibilities. These suggestions would have to have provisions to explain why C affects B, but not A.

Several specific possibilities had been conjured up during in-house discussion of the data. One of these involves the "hair-ball" hypothesis (Reference 11). Acetylene groups first react to form polyenes. However, the addition reaction stops after about six monomers have reacted (Reference 12) because the polyene now is wrapped by the quinoxaline parts and unreacted monomer cannot penetrate to react with the polyene. The result is a hair-ball with a polyene core, and the quinoxaline "hairs" radiating from the center with an unreacted acetylene at the end of each hair. The acetylene on the outside will react, but because of the steric hindrance of the ball, unsaturated moieties like butadiene will be formed

which are less stable than the more conjugated polyene in the core. These products on the surface of the ball can contribute to reaction B, and they can be attacked by oxygen as well at low temperature curing. Mono-functional acetylene terminated sulfone is being scheduled as a resin to test this hypothesis.

Several issues are raised from this study. It is clear that curing in air can impart permanent changes on the AT system as evidenced by the changes in $TgB(\infty)$. More important is how these permanent changes will affect the ultimate properties of the partially cured materials. Works are planned to measure the ultimate properties of ATS as a function of air/nitrogen cure.

Mechanical properties can reveal the effects of the reactions but such experiments are inadequate in shedding lights on the nature of the reactions. Such information, however, is invaluable in fully understanding the cure of the AT technology. The information can also help to enhance the probability of success of any AT resins' development. Other techniques, like spectroscopy, should be employed to explore this area.

The cure effects reported here should be taken into consideration in any experiments relating to the AT systems. Especially true are the experiments designed for correlation purposes. The cure cycles should then be designed in such a way to minimize the confusion from different effects. The question of completeness of reaction should be carefully considered as well.

The fact that the oven-cured specimens do not give good correlation underlines the contention that time and temperature in practical processing procedures are inadequate to describe the cure state of the material after the processing. More appropriate parameters should be considered for this purpose. As an example, the combination of the T_c and $TgB(\infty)$ values can be used to label the cure state from the initial cure. This particular choice of cure state parameters has the drawback that the values may not be unique for all possible cure states.

Reactions C and B are considered as curing reactions here. Cure cycles can be designed to exclude them from the cure. However, for fabricated components exposed in air at their desinged use temperature, these reactions can occur and in such instances they will be considered as aging reactions. So these reactions' effects on properties should be carefully studied and not be ignored.

SECTION V

CONCLUSIONS

Through a series of experiments where the initial curing conditions of the BA-DAB-BA TICA specimens were systematically varied, the effects of curing on dynamic mechanical properties were delineated. The findings can be summarized as follows:

- (1) Two peaks in the a-component were observed in the thermal scans.
- (2) The final Tg (∞) is over 400°C if air is excluded from the cure. Air curing can lower this Tg to below 400°C. Post curing in air at high temperature can increase the final Tg to above 400°C as well.
- (3) Curing in nitrogen had no apparent effect on the second peak of the a-component, but curing in air progressively diminished this peak.
- (4) Three b-component identification points were detected, and they are labeled as Tc, TgA (∞) and Tg B (∞), Tc increases with increasing extent of cure, TgA (∞) is unaffected by any conditions of cure; and curing in air decreases TgB (∞).
- (5) A break in slope in times to b maximum at 250°C was observed. There was no significant difference in the air/nitrogen measurements.

The above findings can be satisfactorily explained through a set of hypotheses which states that four different reactions, or four different reaction effects are present in the AT curing. Two reactions can proceed under nitrogen environment, and are distinguished by their different activation energies. The other two reactions require the presence of air. The one at low temperature will lower the final Tg, while the other at high temperature will have an opposing effect.

The findings in this study should have, directly or indirectly, an impact on most AF related programs. The issues raised and discussed in the discussion section are:

- (1) the effects of the permanent changes caused by the curing on the ultimate properties of the materials,
- (2) the natures of these reactions which should be studied with other techniques,
- (3) the consideration of these effects in designs of cure cycle to avoid confusing results,
- (4) the needs for better parameters to describe the cure states; and
- (5) the possibility of some of these reactions being present during the materials' service life.

Attempts are being initiated, or planned in this laboratory to deal with some of these issues.

REFERENCES

1. R. Kovar, G. Ehlers, and F. E. Arnold, *J. Polym. Sci. Polym. Chem. Ed.*, 15, 1081 (1977).
2. T. E. Helminiak and W. B. Jones, Jr., AFWAL/MLBC, unpublished results.
3. F. L. Hedberg and F. E. Arnold, *J. of App. Polym. Sci.*, 24, 763 (1979).
4. B. A. Reinhardt and F. E. Arnold, AFWAL-TR-80-4012, (1980).
5. J. J. Harrison and C. M. Selwitz, AFML-TR-79-4183, (1980).
6. C. Y-C. Lee, I. J. Goldfarb, and J. D. Henes, AFWAL-TR-80-4159, (1980).
7. C. Y-C. Lee and I. J. Goldfarb, "The Glass Transition Temperature of Partially Cured Polymers as a Non-Equilibrium Parameter and Its Effect on Mechanical Properties" in press.
8. C. Y-C. Lee, AFWAL/MLBP, unpublished results.
9. F. L. Hedberg, C. Y-C. Lee, and I. J. Goldfarb, AFWAL-TR-80-4179 (1980).
10. C. Y-C. Lee, and I. J. Goldfarb, "Tg Determination of Partially Cured Thermosetting Systems" in press.
11. T. E. Helminiak, AFWAL/MLBC, private communication.
12. J. M. Pickard, E. G. Jones, and I. J. Goldfarb, *Macromolecules*, 12, 895 (1979).

TABLE 1. SUMMARY OF THE FOUR-REACTION HYPOTHESIS

<u>Reaction</u>	<u>Conditions</u>	<u>Remark</u>
A	in N_2 ; $< 270^\circ C$	(1) $TgA(\infty) = 260^\circ C$ (2) $TgA(\infty)$ not affected by pre-cure
B	in N_2 ; $> 270^\circ C$	(1) $TgB(\infty) > 400^\circ C$ (2) $TgB(\infty)$ affected by pre-cure (3) decreases a-component
C	in Air; low pump	(1) prohibits B (2) decreases $TgB(\infty)$ (3) no effect on $TgA(\infty)$
D	in Air; $> 350^\circ C$	(1) increases $Tg(\infty)$ (2) decreases a-component

TABLE 2. TABULATION OF b-COMPONENT FEATURES WITH CURING CONDITIONS

<u>Curing Conditions</u>	<u>Tc</u>	<u>TgA(∞)</u>	<u>TgB (∞)</u>
N ₂ /160°C/24h	213°C	260°C	>400°C
Air/160/24	213	260	360
N ₂ /200/1	210	262	>400
Air/200/1	213	257	375
Air/200/1/2	190	258	383
Air/200/2	230	254	370
Air/200/24	--	265	^a 350↑ 362↓
N ₂ /scan	--	263	>400
Air/140/24	180	260	380

Ave. 260 ±5

^a The 350°C value is the b-maximum of the temperature scan-up, and the 362°C the scan-down.